EXPANDED GRAPHITE FORTIFIED MAGNESIA-CARBON REFRACTORIES: FABRICATION AND PROPERTIES

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Submitted by

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CERTIFICATE

This is to certify that the thesis entitled, "**EXPANDED GRAPHITE FORTIFIED MAGNESIA-CARBON REFRACTORIES: FABRICATION AND PROPERTIES**", submitted by **Mr**. **Subham Mahato** carried out in National Institute of Technology, Rourkela, in partial fulfillment of the requirements for the award of Master of Technology Degree in **Ceramic Engineering** at the National Institute of Technology, Rourkela is an authentic work carried out by him under my supervision and guidance.

To the best of my knowledge, the matter embodied in the thesis has not been submitted to any other University/ Institute for the award of any degree or diploma.

I wish him all the success for his future.

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Date: **Subham Mahato**

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Chapter-1

Introduction

1.1 Introduction:

A refractory is defined by ASTM C71 as "nonmetallic materials having those chemical and physical properties that make them applicable for structures or as components of systems that are exposed to environments above 1000^{o}F (538^{o}C)". [1] Refractories have good mechanical properties at high temperature as well as at low temperature. They have good corrosion and erosion resistance to molten slag, metals and hot gases. Due to good thermo-mechanical and thermo-chemical properties refractory materials are used in various high temperature processes like iron and steel making, non-ferrous metal processing, cement, glass, chemical industries etc. They are normally used in high temperature furnaces, kilns, boilers, incinerators etc.

Many scientific and technological inventions and developments would not have been possible without refractory materials. Without the use of refractory manufacturing of any metal is almost impossible. Iron and steel industries are the main consumers of refractory. So, the refractory production has to be in sync with the demand of iron and steel industries. Better manufacturing and application environment is demanding a new generation of refractory material with improved properties, performance and life with eco-friendliness.

Refractories can be classified into three groups based on their raw materials-

a) Acidic (zircon, fireclay and silica)
b) Basic (dolomite, magnesite, magnesia-carbon, alumina/magnesia-carbon, chrome-magnesite and magnesite-chrome)
c) Neutral (alumina, chromites, silicon carbide, carbon and mullite)

Refractories can also be classified into two groups based on the manufacturing process-

a) Shaped refractories (available in the form of different brick shapes and includes the oxide and non-oxide systems)
b) Unshaped refractories (plastic masses, ramming masses, castables, gunning masses, mortars etc.) [2]

Iron and steel industries are the major consumer of refractories. India has emerged as the fourth largest steel producing nation in the world, as per the recent figures release by the World Steel Association in April 2011. Total crude steel production in India for 2010-11 was around 69 million tons and it's expected that the crude steel production in capacity in the country will increase to nearly 110 million tons by 2012-13. Further, if the proposed expansion plans are implemented as per schedule, India may become the second largest crude steel producer in the world by 2015-16. [3] As production of crude steel is increasing at a significant speed, the production of refractory has also increased over the years to meet the growing demand. Besides, there has been a phenomenal change in refractory technology to fulfill the demand of high quality steel production. In this context, carbon containing refractories has found the widest applicability in BOF and EAF furnaces and also in ladle metallurgy due to their good thermal shock resistance and excellent slag-corrosion resistance.

MgO-C bricks have dominated the slag line of ladles for at least a decade as they possess superior slag penetration resistance and excellent thermal shock resistance at elevated temperature because of the non- wetting properties of carbon (graphite) with slag, high thermal conductivity, low thermal expansion and high toughness. [4,5] Increased steel production has lead both refractory manufacturers and users to resume interest on further improvement of thermo-chemical properties of MgO-C refractories. [6]

1.2 MgO-C Refractory:

MgO-C brick is a composite material based on MgO and C and bonded with high carbon containing pitch and resin, with some metallic powder as anti-oxidants to protect the carbon. MgO-C bricks are made by high pressure. These bricks show excellent resistance to thermal shock and slag corrosion at elevated temperatures. MgO-C bricks are used extensively in steel making processes especially in basic oxygen furnaces, electric arc furnaces, lining of steel ladles, etc. [7]

MgO-C bricks have the following features:

1. MgO-C refractories have high refractoriness as no low melting phase occurs between MgO and C.

2. Graphite, the carbon source, has very low thermal expansion; hence in the composite of MgO-C the thermal expansion is low.

3. Graphite has very high thermal conductivity, which imparts high thermal conductivity in the MgO-C composite,

4. Thermal shock resistance of MgO-C is very high because the thermal expansion is low and the thermal conductivity is high.

5. MgO-C bricks prevent the penetration of slag and molten steel because of the non-wettability of carbon.

6. Better ability to absorb stress, thus keeping down the amount of discontinuous wear due to cracks.

MgO-C bricks consist of magnesia, graphite, antioxidant and binder. Magnesia grains are the main constituent of the system which gives very high resistance to basic slag corrosion, but suffer from poor thermal shock resistance. Graphite has non-wetting nature which improves the corrosion and thermal shock resistance of the MgO-C system but it is susceptible to oxidation. Antioxidants prevent oxidation of carbon and improve high temperature strength by the formation of carbides. Binder keeps the different components of the refractory together. Volatile materials from the binder are the first to go out leaving behind carbon.

MgO-C refractories have found the widest applicability in BOF and EAF furnaces and also in steel ladle due to their good thermal shock resistance and excellent slag-corrosion resistance at elevated temperature. These properties come due to the non-wetting nature (graphite) with slag, high thermal conductivity and low thermal expansion of carbon. The penetration and corrosion resistance are improved by the formation of a nascent dense layer of MgO on the working surface of MgO-C brick, due to oxidation of Mg (produced in the reaction between MgO and C). But carbon suffers from poor oxidation resistance and may oxidize to form CO and CO_2 resulting in a porous structure with poor strength and corrosion resistance. Prevention of carbon oxidation is done by using antioxidants, which reacts with incoming oxygen, gets oxidized and protects carbon, thus retaining the brick structure and properties. In presence of high carbon content, conductivity of MgO-C brick increases and results in loss of heat energy through the furnace wall. Presence of large quantities of carbon in MgO-C brick makes the reduction of carbon content in steel difficult. Finally the main problem for nowadays is environmental pollution because the higher amount of carbon produces the higher amount of CO and CO_2 which is released into the atmosphere. So the global aim is to reduce carbon content in MgO-C refractories while retaining the thermo-mechanical properties.

In recent times, several attempts have been made to reduce the carbon content. It has been reported that the presence of nano size particles in MgO-C refractories have improved thermal shock resistance, oxidation resistance and corrosion resistance. In particular, the presence of nano carbon even at low percentages has shown significant improvement of several properties of MgO-C brick. [27] Carbon nanofibers (CNFs) or carbon nanotubes (CNTs) have also been investigated for their use as carbon sources for low carbon refractories due to their unique thermal, mechanical and chemical properties. [8,9] Recently, another new type of nanosized carbon, graphite oxide nanosheets (GONs) was investigated for use as a reinforced phase for the polymer matrix and ceramic matrix composites owing to its excellent mechanical, thermal and electrochemical properties. [10-14] In this study, a different approach has been followed to reduce the carbon content as well as to increase the thermo-mechanical properties and oxidation resistance. In the present work, expanded graphite (EG) was used as a carbon source to partially replace flaky graphite in MgO–C refractories in order to study the effect of its addition on the microstructure and mechanical and thermo-mechanical properties.

1.3 Expanded graphite:

Expanded graphite (EG) is a promising material, which has been widely used as gasket, thermal insulator, fire-resistant composite, etc. Expanded graphite has very high surface area. Generally EG is prepared by rapid heating of graphite intercalation compound (GIC) which results in the abrupt ejection or decomposition of guest molecules and the subsequent huge unidirectional expansion of the initial platelets. Some alternative methods have also been proposed like coupled plasma, laser irradiation and microwave irradiation. [15] Microwave irradiation among these is very promising, because it can be performed at room temperature in a short time with the consumption of lesser energy.

1.4 Application of MgO-C refractory:

Due to their good thermal shock resistance and excellent slag-corrosion resistance at elevated temperature MgO-C refractories have found the widest applicability in BOF and EAF furnaces and also in steel ladle. MgO-C (Magnesia carbon) refractories or Carbon containing Magnesite refractories have been extensively used by steel makers in ladles that are containers for the secondary treatment of steel.

Basic Oxygen Furnace:

MgO-C refractory bricks are widely used in slag lines of BOF (Basic Oxygen Furnace) because of their superior slag-corrosion resistance. The service life of Magnesia-Carbon refractories used in BOFs have been pushed quite significantly (largely due to slag splashing and gunning improvements) even as the service conditions have become more severe due to the increased operating temperature required for continuous casting and the need to produce cleaner steel. [16] These bricks have enhanced the production of steel making by increasing the furnace availability. By using MgO-C bricks clean steel can be produced with less refractory consumption. [17]

Electric Arc Furnace:

Electric arc furnaces are used for melting steel scrap to produce molten metal. MgO-C bricks are applied in most of the lining areas of electric arc furnaces. These bricks are mainly used in hot spots and furnace bottoms, including the slag line. Now a day they have also been used for bottom blowing plugs, the sleeves of furnace-bottom tap holes and furnace bottom electrodes of DC electric furnaces. [18]

Secondary refining furnace:

RH degassers are the most common among various secondary-refining furnaces due to their high refining efficiency and high productivity. The use of MgO-C bricks has been considered for reduced pressure operations. The reaction at lower pressure at high temperatures is more significant. However, slag coating on bricks may eliminate the problems at hot surface. Therefore MgO-C bricks may be usable in furnaces operating under reduced pressure.

Ladle:

A steel ladle is a container for transferring molten steel tapped from the converter or the electric arc furnaces up to the casting shop, reserving the steel during casting and occasionally during secondary refining of the steel. Refractories used for ladle lining must able to withstand the increasing severity of service conditions associated with the secondary steel making in order to produce various grades of steel with stringent specifications. The condition during the steel refining processes is aggressive, which makes the refractory materials used in steel ladles susceptible to a high degree of corrosion. Containing electro-fused magnesia of high purity, MgO-C bricks show excellent corrosion resistance. Furthermore, special additives have been studied for the lining bricks to improve their durability. [19]

MgO-C refractory is one of the highest consumable refractory items in steel sector. The demand for steel in the country is currently growing at the rate of over 8% and it is expected that the demand would grow over by 10% in the next five years. So it is expected that demand of MgO-C refractories will also increase with the demand of steel. Selection of raw materials, their grading and grain size distribution and composition play a very important role in the development of various physical properties, microstructure and thermo-mechanical properties of MgO-C refractory bricks. Various different types of MgO (Magnesite) grains provide different levels of corrosion resistance. Slag corrosion resistance of MgO-C refractories can be improved by the use of fused magnesia grains of high Bulk Density and high purity. [16] Because of its unique advantages and very high demand in steel industry there is a huge scope and requirement of further improvement in the properties of MgO-C refractories.

Chapter – 2

Literature Review

&

Objective of the Present Work

2.1 Historical perspectives of MgO-C refractory:

Carbon has been recognized as a very important component of refractories after 1950's. The addition of carbon results to a better thermal and chemical resistance and hence the life of refractory linings has been increased, which indirectly reduces the cost of steel production. [20, 21] Nowadays carbon containing refractories have been accepted for many different applications. MgO-C bricks are used as an important lining material for basic oxygen furnaces (LD converters), electric arc furnaces (EAF) and also in ladle metallurgy for steel making and refining. [22]

In 1950 pitch bonded dolomite refractories and magnesia carbon brick evolved. It was primarily developed for the basic oxygen furnace. For these refractories carbonization was done during the preheating treatment of the ladle. These refractories showed better thermal–spalling resistance, inhibiting the slag penetration. In 1970 the first zonal lining concept was started. Burned and impregnated magnesia brick was developed with fine pore size to inhibit slag penetration which improved corrosion resistance and thermal spalling. These refractories were applied in charge pad and other high wear and impact areas in basic oxygen furnaces. During this time period for the first time the purity of magnesia became a consideration. Thus Magnesia grain with lime to silica ratio of 2 to 3: 1 and low boron content was used extensively to increase the life of brick by improving the corrosion resistance. In 1980 resin bonded magnesia-graphite brick with higher carbon content was developed. The addition of antioxidants to prevent the oxidation of carbon content and make the brick strong was started during that time period. [23] After 2000 to further improve the corrosion resistance high purity magnesia grains (fused/ sintered) having large crystal size is being used. The type and amount of carbon content are varied to improve the thermal conductivity and oxidation resistance. The addition of various

additives (such as metal, alloy and inorganic compounds) was started to achieve better hot strength, oxidation resistance and corrosion resistance. These additives act as antioxidants and improve the oxidation resistance. It was reported that Al in addition to Si metal powder showed the best oxidation resistance and high temperature strength, whereas Mg alloy containing samples showed the maximum slag corrosion resistance and hydration resistance properties. Oxidation properties were studied in the presence of 2-8, 4-5, 12 and 20% ash content graphite. [24] MgO-C containg graphite with 4-5% ash content was observed to have the best oxidation resistance. Addition of $MgAl_2O_4$ spinel significantly improves slag corrosion and erosion resistance of MgO–C refractory. A study showed that 10 wt% addition of micron sized stoichiometric spinel improves the resistance against oxidation, thermal shock and slag penetration in MgO-C brick particularly in the slag zone of steel ladles. [25, 26]

2.2 Recent advances in MgO-C refractory:

A recent study of nano carbon addition in MgO-C refractory showed that small amounts of nano carbon addition can reduce the carbon content without affecting the other properties. Nano carbon addition also increased the oxidation resistance and the packing density as well as strength. [27] Another study reported an enhancement of 2.2 times in strength for the MgO–C specimen containing 0.4 wt% carbon nano fibres (CNFs) compared to that containing no CNFs, owing to the crack arresting effect of CNFs. [28] Recently, another new study showed the effect of nanosized carbon, graphene or graphite oxide nanosheets (GONs) which was used as a reinforced phase for the polymer matrix and ceramic matrix composites owing to its excellent mechanical, thermal and electrochemical properties. In some previous work GONs were incorporated into MgO–C refractories as a new carbon source to improve the mechanical and thermo-mechanical properties owing to their morphology and high activity. [29]

Graphite has very high thermal conductivity. So, energy loss is greater for MgO-C bricks. In order to reduce the energy consumption due to loss of heat, it is preferred to have relatively low carbon content in MgO-C refractories. [30] But, this leads to lower thermal shock resistance. In recent years, the reduction of carbon content in MgO-C refractories is the main aim of the research. Extensive research is ongoing to reduce the carbon content of MgO-C refractories without deterioration of its properties.

2.3 Raw materials for MgO-C refractory:

The raw materials play a vital role in the performance and life of the refractories. Several research works had been carried out to find out the effect of different raw materials based on purity, crystallite size, porosity and other parameters of different raw materials on the final properties of MgO-C refractories. [31-33] The main raw materials are magnesia, graphite, antioxidants and binder like pitch powder and resin. Details of the each of the raw materials are described below.

2.3.1 Magnesia:

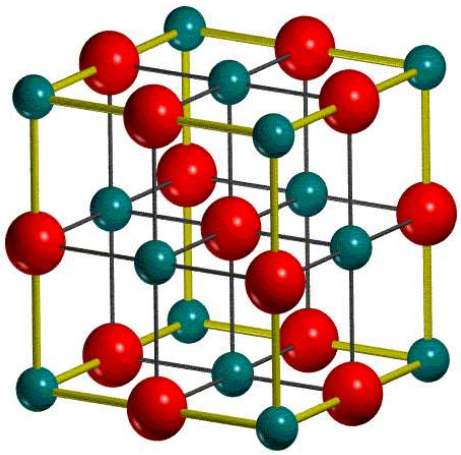

Fig.2.1: Crystal structure of MgO

Magnesia is the main constituent of MgO-C brick which contains about 80 wt% or more of the total batch. Three different types of magnesia raw materials are used to produce MgO-C brick.

i. Sea water magnesia produced by firing $Mg(OH)_2$, extracted from sea water

ii. Sintered magnesia produced from natural magnesite by sintering

iii. Fused magnesia produced by melting magnesia in electric arc furnace

Many research reports have been published on the effect of magnesia aggregates on the corrosion resistance of MgO-C brick. For superior corrosion and abrasion resistance of the final MgO-C brick the magnesia aggregate should have the following characteristics.

i. Large periclase crystal grain to reduce the extent of the grain boundary. [34]

ii. High ratio of CaO/SiO_2 and small content of B_2O_3. [34-36]

iii. High purity and minimum impurity of magnesia.

For the above mentioned reasons fused magnesia grains with high purity and large grain size show better corrosion resistance than sintered magnesia. [37]

2.3.2 Graphite:

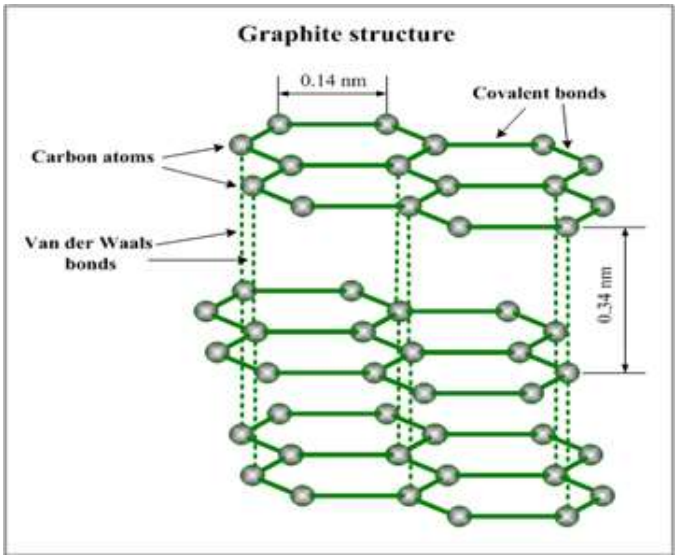

Fig.2.2: Crystal structure of graphite

In MgO-C brick, carbon plays a very important role by providing non-wetting nature to the refractory. Graphite is used as the carbon source because among different commercial sources of carbon, graphite shows the highest oxidation resistance. Carbon gets oxidized in oxidizing atmosphere which results a porous structure with very poor strength. So, resistance against oxidation is very important for the carbon source. Due to the flaky nature of graphite it imparts higher thermal conductivity and lower thermal expansion, resulting in very high thermal shock resistance. Along with the increase of the graphite content the compressibility increases during pressing and results in a decrease in the porosity. Fine graphite particles are more effective to improve the corrosion resistance of refractory. [38] The strength of MgO-C brick particularly during heat treatment has also been reduced by the bigger particle size of graphite. Purity of graphite is also an important factor. Impurities react with MgO and form low melting phase which results in lower corrosion resistance and also lower hot strength. [39]

Graphite's role in MgO-C bricks can be summarized as –

i. Graphite covers the spaces in between magnesia grains and fills the porous brick structure.

ii. Graphite prevents the slag penetration into the brick due to high wetting angle between slag and graphite.

iii. At higher temperature magnesia is reduced to pure magnesium by carbon and the vaporized magnesium comes to the surface of the brick and reoxidized to magnesia. Formation of this dense layer of MgO and CO at the slag- brick interface prevents further penetration of oxygen into the brick.

$$MgO + C \rightarrow Mg + CO$$

$$Mg + {}^{1}/_{2}\, O_2 \rightarrow MgO$$

iv. Graphite improves the thermo – mechanical properties and spalling resistance of the brick because of its high thermal conductivity and low thermal expansion. The size of graphite has also a great role in improving the abrasion, corrosion and oxidation resistance of MgO-C bricks.

v. Slag containing Fe_2O_3 has higher corrosive action than that of containing FeO. Carbon reduces Fe_2O_3 to FeO and further reduction of FeO produces metallic iron, enriches the production of steel.

$$Fe_2O_3 + C \rightarrow 2FeO + CO \uparrow$$

$$FeO + C \rightarrow Fe \downarrow + CO \uparrow$$

2.3.3 Resin:

Because of flaky and non-wetting characteristics of graphite, it is very difficult to produce a dense brick without any strong binder. In the early days pitch was used as binder for MgO-C brick. But during operation pitch releases large amounts of volatile matters, which are very toxic due to their high content of polycrystalline aromatic compound (PAC) like benzo-alpha-pyrenes. Also to use pitch hot pressing of the mixture was necessary. So, resin was found to be the best binder for MgO-C refractories because of these following properties-

i. Resin contains high amount of fixed carbon which gives strong bonding property.
ii. Resin has a high chemical affinity towards graphite and magnesia grain.
iii. Because of its thermosetting nature resin possesses high dry strength.
iv. It produces less hazardous gas than tar/ pitch.
v. At curing temperature (~ $200^{o}C$) resin polymerizes which gives isotropic interlocking structure.
vi. Cold crushing strength (CCS) increases with the increase of resin content.

The desired viscosity of resin should be around 8000 cps, which ensures proper mixing of the other raw materials. Viscosity of resin is quite sensitive to temperature which increases with decrease in temperature. So, in winter viscosity of resin increases, which causes low dispersion of ingredients in the mixer machine. Whereas in summer due to high temperature viscosity decreases which gives less strength in the green body and creates lamination. Powder novalac resin is normally used to overcome this type of difficulty. [40] Compressibility during pressing improves with the increase in resin content and consequently the CCS of the tempered samples increase. The resol type resin is best as binder among various resin types. Because of its lower

viscosity and lower content of volatile species the samples containing resol had the lowest porosity after heating at high temperature.

2.3.4 Antioxidants:

The main problems of using MgO-C bricks are the lower oxidation resistance as well as the poor mechanical strength of graphite which causes loosening of the constituents at high temperature leading to reduced wear resistance as well as resistance to chemical corrosion. The oxidations of carbon in MgO-C refractories happen in two ways (a) direct oxidation and (b) indirect oxidation. Direct oxidation occurs below 1400^{o}C and carbon is oxidized directly by atmospheric oxygen. Indirect oxidation occurs above 1400^{o}C and carbon is oxidized by the oxygen from MgO or slag. The resulting Mg vapor oxidizes again above 1500^{o}C and generates MgO which is called the secondary oxide phase or the dense layer. This dense layer gives rise to resistance to further oxidation. [41-43]

$$2C_{(S)} + O_{2\,(g)} = 2CO_{(g)}$$

$$C_{(S)} + MgO_{(S)} = Mg_{(g)} + CO_{(g)}$$

$$2Mg_{(g)} + O_{2\,(g)} = 2MgO_{(s)}$$

Thus to prevent oxidation of carbon, different antioxidants such as Magnesium (Mg), Aluminum (Al), Silicon (Si), Boron Carbide (B_4C) are used in MgO-C refractories. Due to lower cost and higher effective protection Al and Si antioxidants are mostly used.

During the operation Al metal reacts with O_2 and forms alumina in the form of a fine layer. At the melting temperature of aluminium (660^{o}C), liquid aluminium breaks the layer of alumina and reacts with surrounding carbon to form aluminium carbide.

$$2Al_{(s)} + 3O_{2\,(g)} \rightarrow Al_2O_{3\,(s)}$$

$$4Al_{(l)} + 3C_{(s)} \rightarrow Al_4C_{3\,(s)}$$

At a temperature higher than 1000^{o}C Al_4C_3 reacts with CO to form Al_2O_3. Alumina directly reacts with surrounding magnesia and forms MgO-Al_2O_3 spinel. [44, 45]

$$Al_4C_{3\,(s)} + 3CO_{(g)} \rightarrow 2Al_2O_{3\,(s)} + 9C_{(s)}$$

$$MgO_{(s)} + Al_2O_{3\,(s)} \rightarrow MgO\text{-}Al_2O_{3\,(s)}$$

B_4C performs much better oxidation resistance than Al. B_4C reacts with CO to form B_2O_3. Then this B_2O_3 reacts with MgO and produces a liquid phase compound MgO.B_2O_3. [46]

$$B_4C_{(s)} + 6CO_{(g)} \rightarrow B_2O_{3\,(l)} + 7C_{(s)}$$

$$B_2O_{3\,(l)} + 3MgO_{(s)} \rightarrow Mg_3B_2O_{6\,(s)}$$

In this way B_4C protects the carbon of MgO-C bricks and improves the life.

2.4 Expanded graphite:

The exfoliation of graphite is a phase transition involving the vaporization of the intercalate in the graphite. Expanded graphite (EG) is a well-known material usually produced from various intercalation compounds submitted to a thermal shock. EG are normally prepared from flaky particles of acid-based complexes passing throughout the flame of a burner. Since the intercalate is suddenly volatilized, a huge unidirectional expansion of the starting intercalated flakes occurs. A kind of black snow made of pure graphite worms is recovered. Expanded graphite (EG) has numerous actual and potential applications, such as supports for various dispersed matters, and for uses in gasketing, adsorption, electromagnetic interference shielding, vibration damping, thermal insulation, electrochemical applications and stress sensing. Because of such a number of applications, EG is a material of growing technological importance. [47]

The material has a wide range of applications, such as

- The compression of expanded graphite particles in the absence of a binder results in a flexible sheet material which is useful for high-temperature gaskets.
- A refractory sealing material can be formed by adding a binder and expanded graphite to a refractory aggregate and heating it to yield a non-porous sealing layer.
- Expanded graphite is commercially available as a fire extinguisher agent.
- Expanded graphite is also commercially available as a thermal insulator, particularly one for molten metals.
- Expanded graphite can serve as a chemical reagent with higher reactivity than natural graphite.

The exfoliation of graphite is a process in which graphite expands up to hundreds of times along the c axis resulting in a puffed-up material with a low density and a high temperature resistance.

Fig.2.3: Image of expanded graphite

2.4.1 Exfoliation techniques:

Exfoliation is mainly done by rapid heating or flash heating of graphite intercalation compounds. Due to the sudden volatization of intercalate a huge unidirectional expansion occurs. There are several techniques to exfoliate graphite.

Wen-Shyong Kuo et al. used a mixture of concentrated sulfuric acid and nitric acid (4:1, v/ v) as intercalate agent which was mixed with graphite flake at room temperature. The reaction mixture was stirred continuously for 16 h. The acid-treated natural graphite was washed with water until neutralized and was then dried at 100^{o}C to remove any remaining water. The dried particles were heat-treated at 1050^{o}C for 15s to obtain expanded graphite particles with a "c" dimension about 300 times that of the original "c" direction dimension. [49]

Zhang Shengtao et al. used potassium permanganate and formic acid to intercalate the graphite together with sulfuric acid and nitric acid. Heating temperature was also varied from 800^{o}C to 900^{o}C. [50]

Eduardo H.L. Falcao et al. have reported the exfoliation of graphite by microwave heating. Potassium-THF (tetrahydrofuran) was used to intercalate the graphite. Graphite and potassium were heated in an evacuated, flame-sealed glass tube to afford KC_8 which was transferred to flasks containing THF. Then it was soaked for 4–24 h and sonicated for about 1 h. The resulting black solid was filtered, dried (~70^{o}C) and transferred to glass tubes which were heated at high power in a commercial MW oven to obtain expanded graphite. [51]

A.Yoshida et al. have reported difference in morphology between the exfoliated graphites produced by five different intercalation compounds (GICs) with H_2SO_4, $FeCl_3$ & Na tetrahydrofuran (THF), K-THF and Co-THF from flaky natural graphite powder with the average particle size of 400 μm. [52]

Beata Tryba et al. have reported the exfoliation of two residue compounds with H_2SO_4 under microwave of different powers. The first residue compound was prepared through electrochemical intercalation (anodic oxidation) of H_2SO_4 with an electric power consumption of 7.7 A h/kg, followed by water rinsing and the second residue was prepared through washing the intercalation compound synthesized in concentrated H_2SO_4 with H_2O_2 at room temperature (chemical intercalation). [53]

Tong Wei et al. have reported a rapid and efficient method to prepare exfoliated graphite by microwave irradiation. Unlike previous reported methods, the natural graphite (NG), oxidant

($KMnO_4$) and intercalation agent (HNO_3) were only simply mixed before MW irradiation, and the intercalation and exfoliation were all accomplished in 60s under MW irradiation. [54]

Among all the techniques, MW irradiation is very promising, because it can be performed at room temperature in a short time with the consumption of less energy.

2.5 Objective of the present work:

MgO–C refractory is a crucial item for steel production which possesses many advantages as a furnace lining. But, there are several problems still to be resolved. Therefore enormous scope of further research and development still exists in this field. In recent times, the main aim of research is to reduce carbon content in MgO-C refractories while retaining all the good properties. A lot of attempts have been made to reduce the carbon content while retaining the benefits of a high carbon MgO-C refractory.

Because of good thermal shock resistance and excellent slag-corrosion resistance at elevated temperature MgO-C bricks have found the widest applicability in BOF and EAF furnaces and also in steel ladle. Graphite fills the pores of MgO-C brick and improves the non-wetting property of the bricks and thereby improves the slag corrosion resistance. But higher amounts of graphite impose several difficulties such as high thermal conductivity and relatively low strength particularly at high temperatures because of high rate of oxidation of graphite. However, the main area of concern is the environmental pollution due to the produced CO and CO_2 during oxidation of these bricks.

In this study, a different approach has been followed to reduce the carbon content as well as to increase the thermo-mechanical properties and oxidation resistance. In this study expanded graphite has been chosen to partially substitute the graphite phase in MgO-C refractories. Small amounts of expanded graphite have been used to partially replace the graphite phase in a conventional MgO-C brick formulation and a few selected properties have been measured. An important aspect of this work is the fabrication of the refractory specimens in plant conditions with characterization and property evaluation being done as done with industrial specimens.

Chapter-3

Experimental Work

3.1 Raw materials:

Commercially available high quality with low impurity fused magnesia (FM), natural flakes graphite, aluminium metal powder (- 150 µm), boron carbide powder and expanded graphite were used to maintain the granulometry of the mixture. Liquid resin and resin powder were taken as additives of base raw materials for the fabrication of low carbon graded MgO-C brick.

As mentioned earlier, this research work is centered around the preparation of expanded graphite to use in MgO-C refractory as partial replacement of graphite.

In this present work, high purity magnesia, FM 97 was taken as the raw material for fused magnesia, considering the selection criteria like purity, CaO/SiO_2 ratio, low Fe_2O_3 content and large crystals in the range of 500-1500 µm. [55, 56] High purity graphite, 97 FC, was taken as a raw material for carbon and resol resin (novalac type) was used as binder. The chemical properties of magnesia, flake graphite and liquid resin are given in the tables below.

Table.3.1: Chemical composition in percentage of fused magnesia:

Raw materials	MgO (%)	Al_2O_3 (%)	SiO_2 (%)	CaO (%)	Fe_2O_3 (%)	Na_2O (%)
Fused magnesia	97.10	0.07	0.40	1.40	0.50	0.50

Table.3.2: Chemical analysis of flake graphite:

Raw materials	Carbon (%)	Volatile matter (%)	Ash (%)
Flake Graphite	97.05	0.69	2.26

Table.3.3: Physical and chemical analysis of liquid resin:

Properties	**Liquid resin**
Viscosity (CPS) at 25^{o}C	8500-9000
Specific gravity at 25^{o}C	1.23
Nonvolatile matter (%)	80.10
Fixed carbon (%)	47.85
Moisture (%)	~ 4.0

3.2 Fabrication of MgO-C brick:

The expanded graphite was used to replace a part of the graphite phase for the preparation of a limited number of MgO-C refractory bricks.

3.2.1 Batch preparation:

Different batches of MgO-C brick were prepared by taking the same amount of MgO, resin and anti-oxidant contents. However, Different compositions of MgO-C bricks have been fabricated using different amounts of expanded graphite as partial replacement of the natural flake graphite. All the batches were prepared under identical conditions. All the variations done in the study are compared with the conventionally used MgO-C brick composition prepared under similar conditions. Compositions of different batches are listed in the following table:

3.2.2 Mixing:

The purpose of mixing the raw materials is to make a refractory batch and transform all the solid components and the liquid additions into a macro homogeneous mixture that can be subsequently molded or shaped by one of the numerous fabrication methods employed by modern refractory manufacturers**.** All the above batches were separately mixed in a pan mixer at room temperature for a period of 45 minutes. All the solid raw materials and liquid additives are mixed in a sequence to get a macro homogeneous mixture.

3.2.3 Aging:

After homogeneously mixing of the materials, the batches were kept for 2 hour for ageing. During aging the polymerization of resin takes place by developing carbon carbon bonds.

3.2.4 Pressing:

The mixed materials after aging were compacted to give a desired shape by pressing. The aged mixtures were pressed uniaxially by hydraulic press in a steel mold. An appropriate weight of each mixture was taken to get the desired green density and the size of the brick. The steel mold was cleaned using cotton and brush after each pressing. To avoid stickiness between the mixture and mold, kerosene was used as a lubricating agent. The mixtures were charged slowly into the mold cavity and leveled uniformly in order to avoid lamination in the pressed bricks.

3.2.5 Tempering:

Tempering is the heat treatment process of the refractories at low temperature to remove volatile matters from the organic green binders and to impart enough green strength for handling. By this process the chemical bond is developed in the refractory grains and the bonding phase. Tempering of the pressed green bricks was done at $200^{o}C$ for 12 hours. With the increase in temperature phenolic resin got converted to carbonaceous phase which helped in developing a stronger carbonaceous bond for the refractory brick and increased the mechanical strength of the brick.

3.2.6 Coking:

After tempering the bricks were cut into different pieces having different sizes for the purpose of different testing. Coking was carried out at 1000^{o}C for 4 h under reducing atmosphere (carbon bed).

3.3 Characterizations and measurement techniques:

3.3.1 Phase analysis:

Phase analysis of the samples was carried out by standard powder x-ray diffraction technique using Cu K_{α} radiation with a step-scanning speed of 227^{o}/min. Diffraction patterns were analyzed by X'pert HighScore software. Intensity ratios were calculated from the digital counts for the relevant peak positions (highest peaks of each of the phases)**.**

3.3.2 TGA analysis:

Thermal analysis of the samples was carried out primarily to determine the oxidation temperature of graphite and also to measure the amounts of residue, which has been assumed to the quantity of silicon carbide contained in each of the samples prepared in this investigation. For this purpose, a small quantity of the sample was subjected to TGA analysis in flowing air atmosphere with a heating rate of 5^{o}C/minute.

3.3.3 CHN analysis:

CHN analysis measures carbon, hydrogen and nitrogen elemental content in a wide range of sample matrices, sizes and concentrations, with accuracy and precision. It is a rapid, accurate, inexpensive composition and purity test. Typically, 1.0 to 3.0 mg is enough for an analysis with a detection limit of 0.02% when analyzing for Carbon, Hydrogen and Nitrogen. In its simplest form, simultaneous CHN analysis requires high temperature combustion in an oxygen-rich environment.

3.3.4 Micro-structural analysis of the composite by SEM:

Microstructures of natural flake graphite, expanded graphite were studied using standard Scanning Electron Microscopes (JEOL-JSM 6480LV). The accelerating voltage was 15/20 kV. The powders were fixed on a self-adhesive carbon tape. For micro-structural analysis of MgO-C samples we cut thin pieces from the bricks. Then those thin slices of samples were polished by various grades of abrasive papers and diamond paste.

3.3.5 Apparent porosity (AP) and bulk density (BD):

AP is defined as ratio of the total volume of the closed pores to its bulk volume and expressed as a percentage of the bulk volume. Closed porosity is the pores that are not penetrated by the immersion liquid, whereas open porosity are those pores which are penetrated by the immersion liquid. AP was measured as per the standard of IS: 1528, Part-8 (1974) both for tampered and coke samples. The Archimedean evacuation method generally measures both bulk density and apparent porosity.

The test samples were cut from the tempered bricks. After taking dry weight all the samples were put into a container and water was added. Then the container was heated for 2 hrs. So that all the open pores are filled with water. After that, the suspended weight (W_2) and soaked weight (W_3) were taken and AP was calculated as follows:

$$AP = (W_3-W_1) / (W_3-W_2) \times 100$$

BD is the ratio of the mass of the dry material of a porous body to its bulk volume expressed in gm/cm^3 or kg/m^3, where bulk volume is the sum of the volumes of the solid material, the open pores and the closed pores in a porous body. BD was measured as per the standard of IS: 1528, Part -12 (1974) both for tampered and coke samples.

Whereas true density is the ratio of mass of the material of a porous body to its true volume and true volume is the volume of solid material in a porous body.

$$B.D = (W_1/W_3-W_2) \times \text{density of liquid at temperature of test}$$

(e.g. density of water at 25^oC : 0.997044 gm/cc, at 30^oC : 0.995646 gm/cc)

3.3.6 Cold crushing strength (CCS):

Cold crushing strength of refractory bricks and shapes is the gross compressive stress required to cause fracture. The cold crushing strength of the tempered and coked samples was measured as per ASTMC-133. The test samples were cut from the standard brick samples. Cold crushing strength of the refractories is measured by placing a suitable refractory specimen of on flat surface followed by application of uniform load to it through a bearing block in a standard mechanical or hydraulic compression testing machine. The load at which crack appears in the refractory specimen represents the cold crushing strength of the specimen. The load is applied uniformly on the sample in the flat position. It is expressed as kg/cm^2.

The working formula for calculating CCS is given by,

$$CCS = Load/Area\ (kg/cm^2)$$

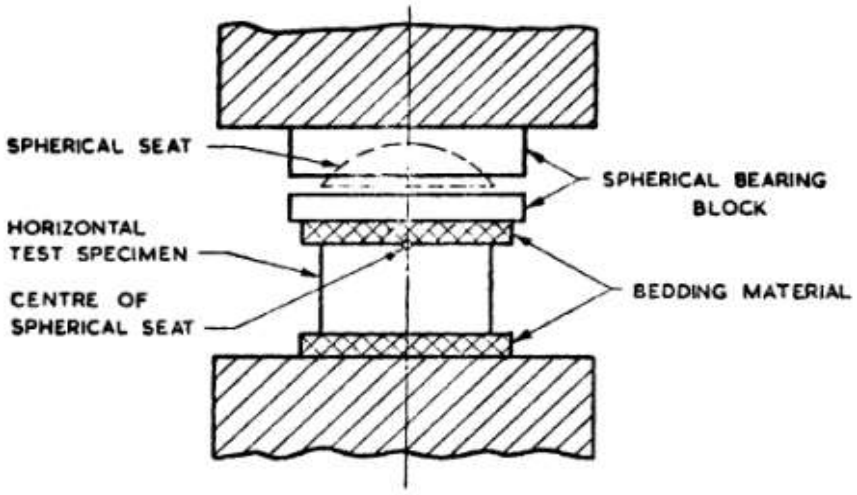

Fig.3.1: Schematic diagram of CCS

3.3.7 Hot modulus of rupture (HMOR):

The modulus of rupture of refractory specimen is determined as the amount of force applied to a rectangular test piece of specific dimensions until failure occurs. This test method covers the determination of the modulus of rupture of carbon-containing refractories at elevated temperatures in air. It was determined as per ASTM C133-7. Each value of HMOR was the average of two parallel specimens. It was done by three - point bending test using HMOR testing apparatus. All the specimens for HMOR were taken as 150mm × 25 mm × 25 mm without pre - firing at air atmosphere. The final temperature of HMOR was 1400^{o}C with a heating rate of heating rate of 5^{o}C/min. It was done in air atmosphere with a soaking time of 30 min. Finally, the loading rate of HMOR was 1.2-1.4 kg/s according to samples.

The HMOR value was calculated by the following formula:

$$HMOR = (3\ W \times L) / (2\ b \times d^2)$$

Where "W" (kg) is the maximum load when the specimen is broken;

"L" is the span length between the lower supporting points. (125 mm for all the tests in the work);

"b" is the breadth (cm), "d" is the height of the specimen (cm).

3.3.8 Modulus of elasticity (MOE):

MOE was measured by the ultrasonic method in which the propagation speed of ultrasonic waves was measured along the length of tempered samples of 150×25×25 mm. Ultrasonic pulse velocity testing (UPVT) was first reported being used on refractory materials in the late 1950's. Briefly, pulses of longitudinal elastic stress waves are generated by an electro acoustical transducer that is held in direct contact with the surface of the refractory under test. After travelling through the material, the pulses are received and converted into electrical energy by a second transducer.

Most standards describe three possible arrangements for the transducers:

(1) The transducers are located directly opposite each other (direct transmission).

(2) The transducers are located diagonally to each other; that is, the transducers are across the corners (diagonal transmission).

(3) The transducers are attached to the same surface and separated by a known distance (indirect transmission).

The velocity, V, is calculated from the distance between the two transducers and the electronically measured transit time of the pulse as, V (m/s) = L / T

Where L is the path length (m) and T is the transit time (s).

By determining the bulk density and ultrasonic velocity of a refractory material, it is possible to calculate the dynamic modulus of elasticity using the equation below:

$$MOE = \frac{\rho V_s^2 (V_p^2 - 4V_s^2)}{(V_p^2 - V_s^2)}$$

From this we can also measure bulk modulus and shear modulus by using the following equations,

$$Bulk\ modulus = \frac{\rho(V_p^2 - 4V_s^2)}{3}$$

$$Shear\ modulus = \rho V_s^2$$

Where V_s is the pulse velocity (m/s), V_p is the shear velocity (m/s) and ρ is the bulk density (kg/m^3)

3.3.9 Oxidation resistance:

Oxidation resistance of the fabricated bricks was tested on cube shaped samples. The samples were fired in an electrical furnace at 1400^{o}C for 10 hours in air atmosphere. At this temperature all the carbonaceous materials of the brick got oxidized particularly from the outer surface. The color of the oxidized portion turned off-white compared to the black color of the virgin brick and therefore the boundary between the un-oxidized and the oxidized regions were quite evident. After the heat-treatment, the cuboid shaped samples were cut and the diameter of black portion was measured at different locations and the average value was taken.

Oxidation index is determined by the formula:

Oxidation index = (Area of oxidized zone / Total area) × 100

Lower oxidation index indicates the higher oxidation resistance of the brick.

It may be noted that conventionally the oxidation resistance tests are carried out by firing the samples at 1400^{o}C for 5 hours. However we have used a much more stringent test standard for measuring oxidation resistance of our specimens.

3.3.10 Thermal shock resistance:

Thermal shock/thermal spalling is the direct result of exposing the refractory installations to rapid heating and cooling conditions which cause temperature gradients within the refractory. Such gradients cause an uneven thermal strain distribution through the sample, may cause failure of the material. [57, 58] The standard method of finding out spalling resistance is heating the material at an elevated temperature followed by sudden cooling in air at ambient temperature. The thermal shock resistance of refractory materials is determined using standard quench tests [59, 60] in which the material is heated and cooled subsequently and the number of heating & cooling cycles that a material can withstand prior to failure is taken as its thermal shock resistance. The quantification was done by the number of cycles to withstand such temperature fluctuations. The sample specimens were cut from tempered bricks. These samples are heated at 1400ºC for 10 minutes and then suddenly brought down to ambient conditions by cooling it in the air for 10 minutes. The number of cycles before any crack in the specimen was noted down as the thermal shock resistance.

Chapter – 4

Results & Discussion

4.1 Structure and chemistry of graphite and expanded graphite:

An investigation of natural graphite was done by using different experimental techniques like SEM and XRD. Natural graphite was characterized were characterized from the points of view of their particle size, crystallinity, purity etc.

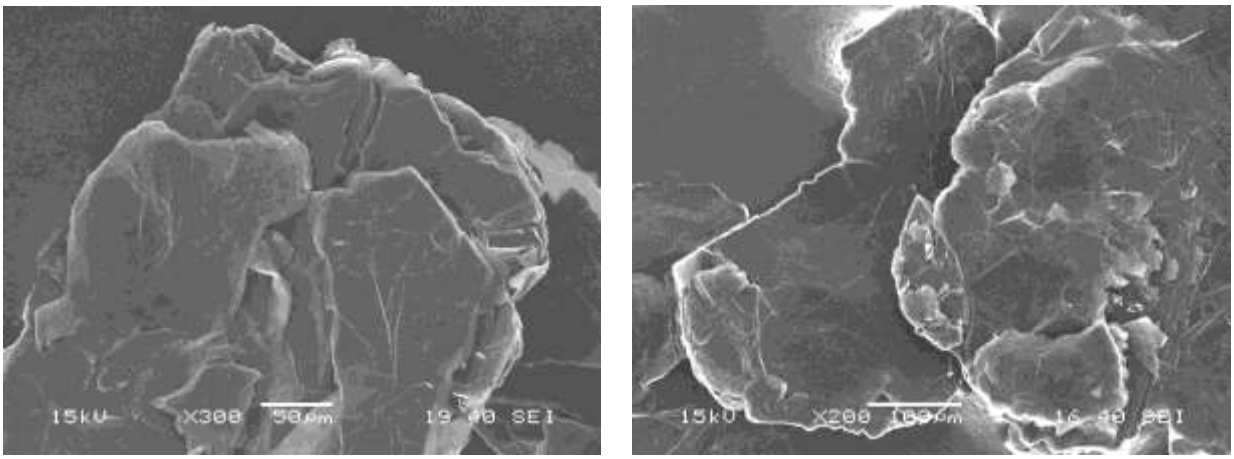

Fig.4.1: SEM images of natural graphite

From SEM images it was observed that natural graphite is flaky in nature and the graphene layers are attached together. From the SEM images it was also observed that the dimension of graphite flakes is more than 200 µm.

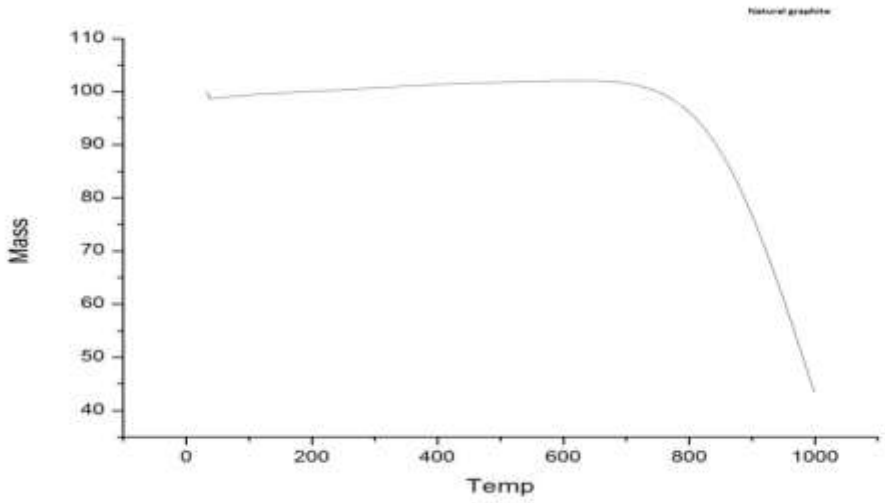

Fig. 4.2: Thermal analysis of the natural flake graphite (97FC) sample

Thermal analysis was done in flowing air atmosphere up to a temperature of 1000^{o}C at 10^{o}C/min. Results of TGA analysis of natural flake graphite samples are presented in Fig.4.2. As expected severe oxidation took place and consequently weight loss occured. However, the process was not complete upto 1000^{o}C (weight didn't become constant). Still from the graph we can have an idea that almost 85-90% graphite was oxidized at that temperature range.

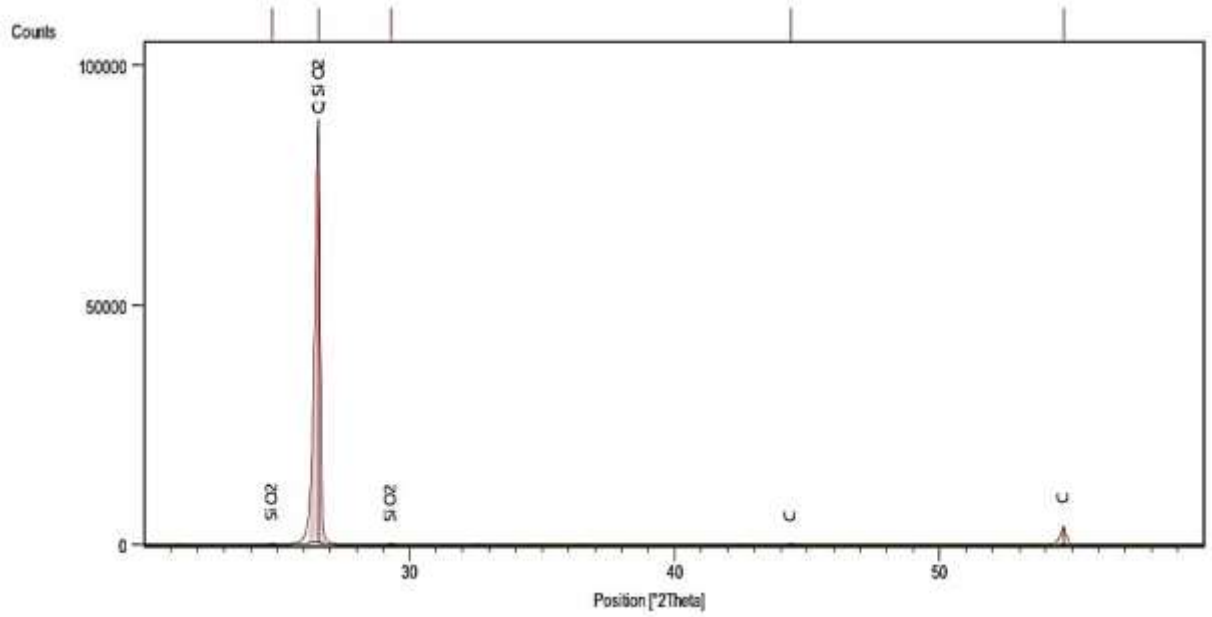

Fig.4.3: XRD pattern of graphite

XRD patterns of natural graphite are presented in Fig.4.3. From the XRD pattern it can be seen that there was some silica impurities present already in the natural graphite. The peaks at 26.56^{o} and 54.69^{o} is consistent with the (002) and (004) peaks of graphite respectively.

A detail characterization of expanded graphite was done by SEM, XRD and CHN test.

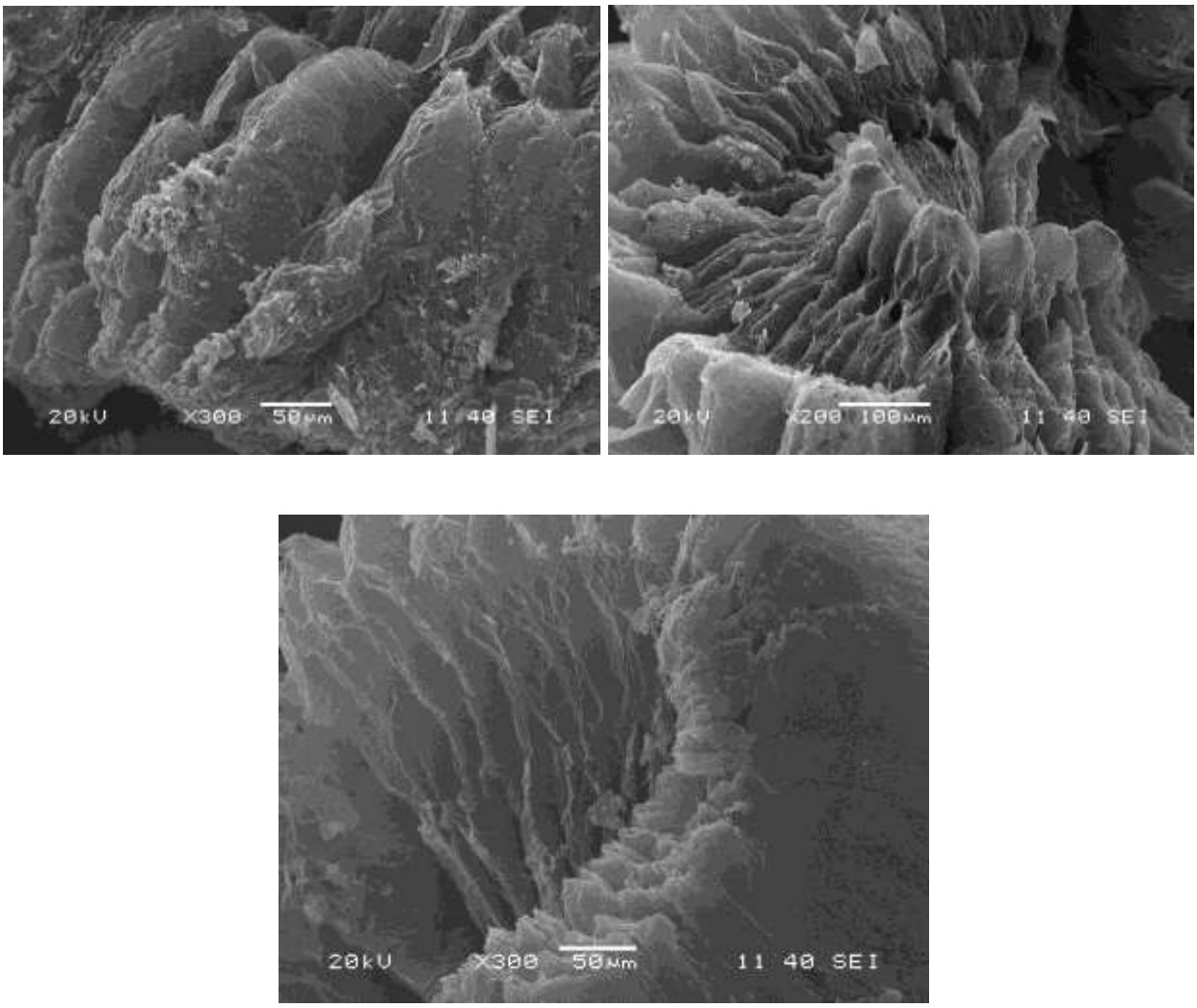

Fig. 4.4: SEM images of expanded graphite

From the SEM images of expanded graphite it was clear that the natural graphite was expanded. After exfoliation the graphite flakes are expanded perpendicular to the graphene layers and gives a warm like structure. Spacing between the graphene layers increased upto 30 µm and exposed.

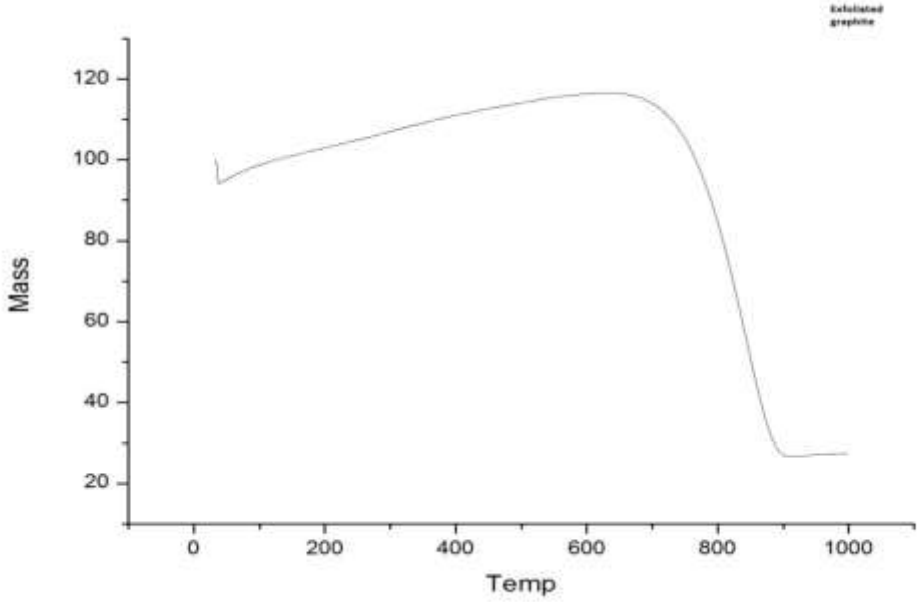

Fig.4.5: Thermal analysis of the expanded graphite

Conditions of thermal analysis were same as the natural graphite. Results of TGA analysis of natural flake graphite samples are presented in Fig.4.5. The result is almost similar to the natural graphite. But the weight loss started at lower temperature due to high reactivity of expanded graphite. The oxidization process was completed around 900^{o}C.

From the CHN test we also determined the carbon percentage present in the expanded graphite. The result of CHN test is given in the following table.

Table 4.1: Weight percentage of carbon, hydrogen & nitrogen in expanded graphite:

Sample name	Carbon (%)	Hydrogen (%)	Nitrogen (%)
Expanded graphite	73.56	4.47	2.14

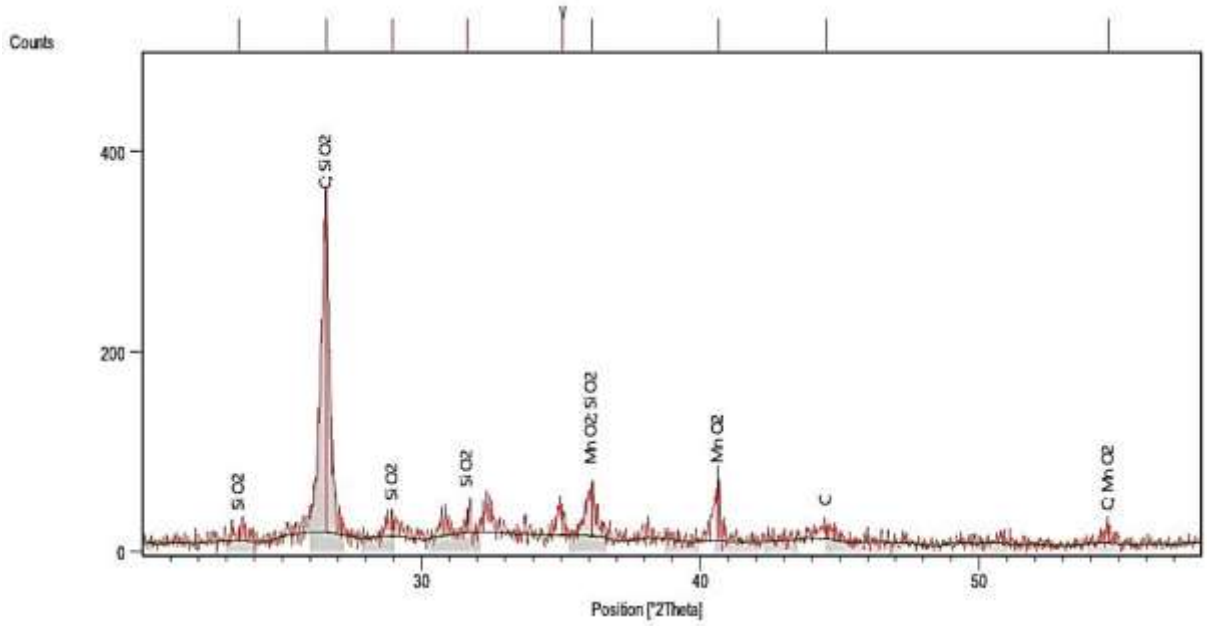

Fig.4.6: XRD pattern of expanded graphite

XRD pattern of expanded graphite is similar to the natural graphite except some extra impurity peaks which came due to the presence of manganese oxide. There's a lot of difference in the peak intensities. Natural graphite shows a great, sharp and symmetrical peak shape because of its high crystallinity. After oxide intercalation, crystal defects increase. As a result crystallinity decrease and diffraction peak intensity decrease.

4.2 Physical and mechanical properties:

4.2.1 Physical properties:

4.2.1.1 Apparent porosity, Bulk density and Cold crushing strength (before coking):

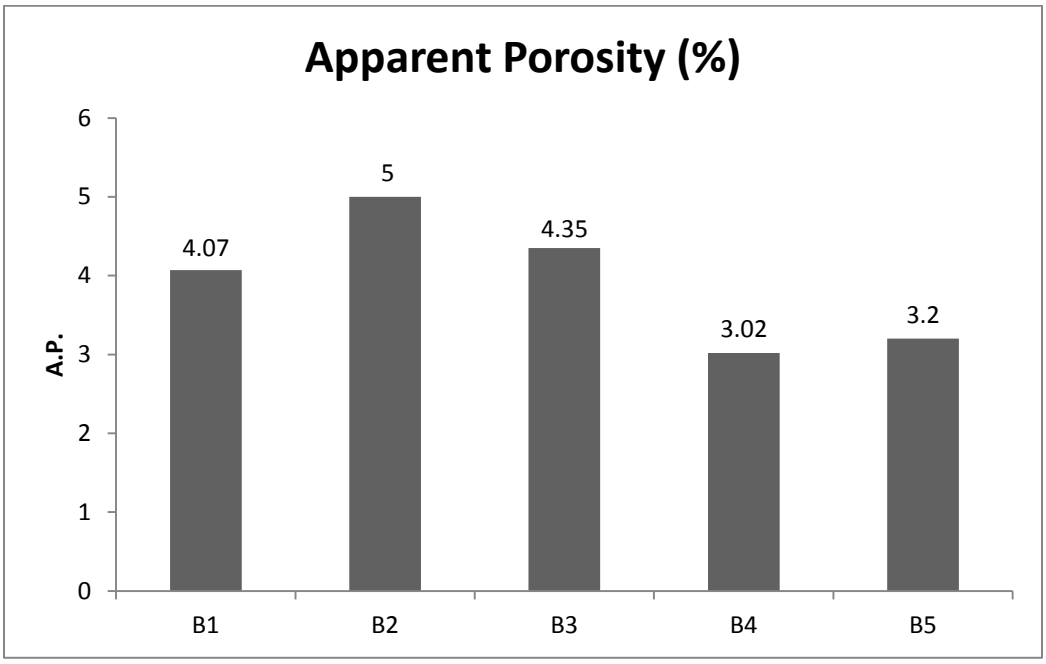

Fig.4.7: Variation of apparent porosity with the variation of expanded graphite content

The change in AP with the increase of expanded graphite is shown in fig.4.7. With the addition of expanded graphite the percentage of AP is reducing. The AP varies in the range of 3.02 to 5 wt%. AP has the value of 4.07 wt% for B1 and has the value 3.02 for B4. This decrease in AP is because of addition of expanded graphite increases the filling of spaces between bigger refractory particles. Thus overall the porosity decreases. But in case of B5 expanded graphite AP increases again.

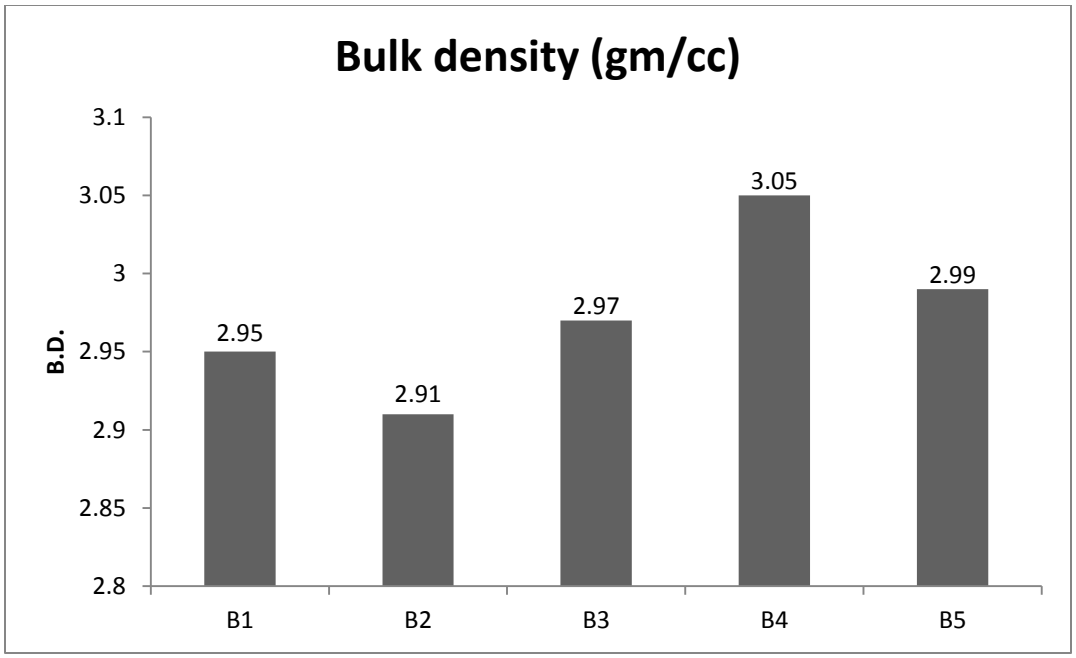

Fig.4.8: Variation of bulk density with the variation of expanded graphite content

The variation of bulk density is shown in fig.4.8. The variation of bulk density with the expanded graphite is very less which ranges from 2.91 gm/cc to 3.05 gm/cc. The bulk density for B1 was 2.95 gm/cc. With the increase of expanded graphite content better pore filling is done which results in a higher bulk density. But as the pore filling is done for B4 so, bulk density decreases again with further addition of expanded graphite.

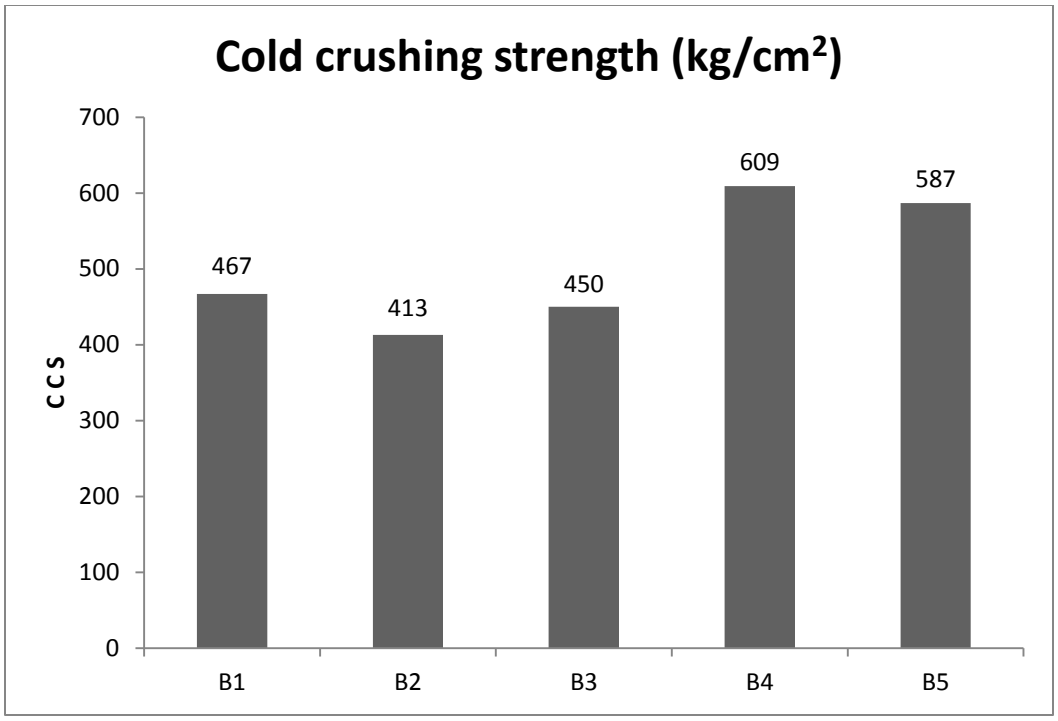

Fig.4.9: Variation of cold crushing strength with the variation of expanded graphite content

The variation of cold crushing strength with the expanded graphite is shown in fig.4.9. From the figure it is clear that with the increase of expanded graphite cold crushing strength increases. The CCS value of the sample which contains no expanded graphite is 467 kg/cm^2 but for B4 sample CCS value is 609 kg/cm^2. But the CCS value remains almost same after B4 sample. Increase in CCS is because of the increase of expanded graphite which causes better filling of pores and results in an increase in BD. But for B4 best pore filling is achieved. So, further addition of expanded graphite does not affect the CCS value much.

4.2.1.2 Apparent porosity, Bulk density and Cold crushing strength (after coking):

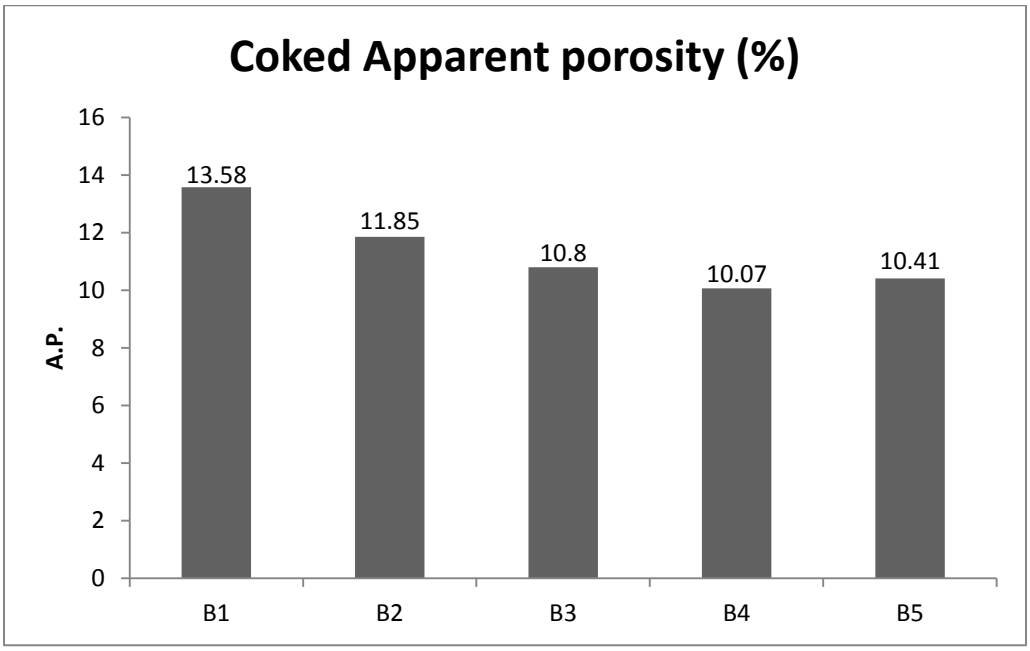

Fig.4.10: Variation of coked apparent porosity with the variation of expanded graphite content

The variation of apparent porosity of coked bricks is shown in fig.4.10. With the addition of expanded graphite the percentage of AP is reducing in similar fashion to AP of the bricks before coking while B4 brick gives the best value. The AP varies in the range of 13.58 to 10.07. The coked AP value of the B1 brick has increased more than other bricks. AP values of coked bricks increase because of the burning out of the total organic portion of the resin. Due to the burn out of the resin pores are created within the bricks which increase porosity.

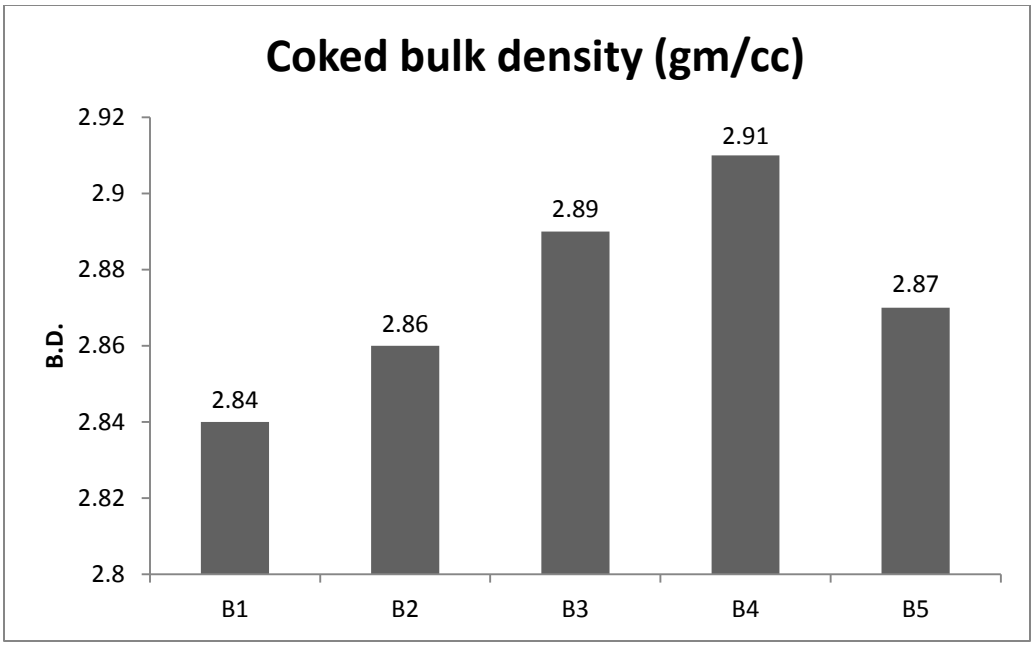

Fig.4.11: Variation of coked bulk density with the variation of expanded graphite content

The change in bulk density of coked bricks is shown in fig.4.11. The values of bulk density vary from 2.84 gm/cc to 2.91 gm/cc. The values decrease in comparison with bulk density of tampered bricks. This is because of the same reason of burn out of resin during coking. Similar to the previous tests here also the B4 brick shows the best value which is 2.91 gm/cc.

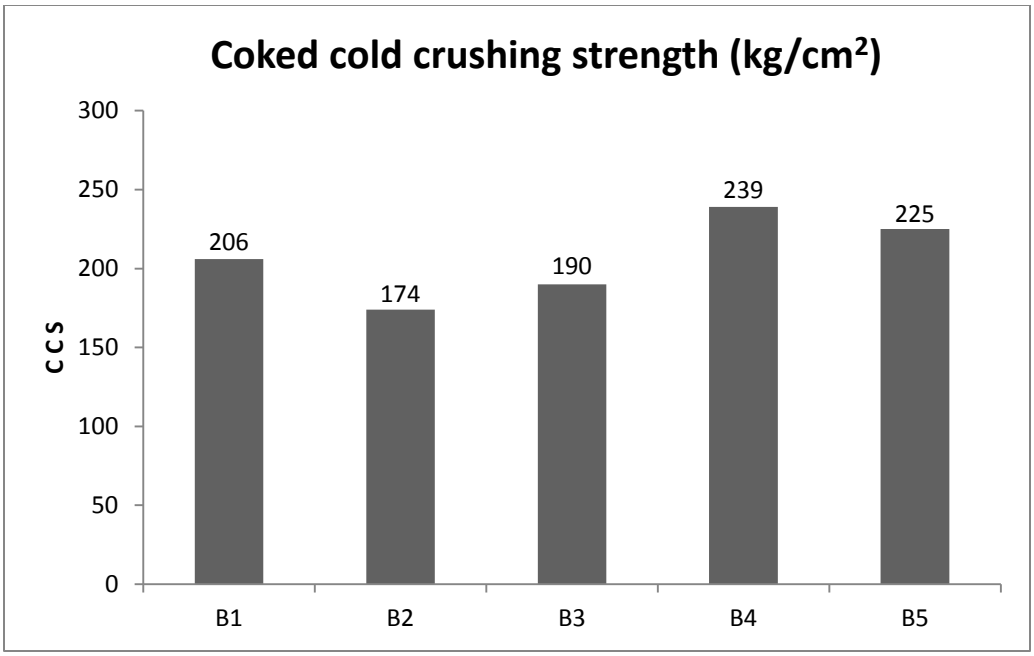

Fig.4.12: Variation of coked cold crushing strength with the variation of expanded graphite content

The coked CCS values are shown in fig.4.12. The CCS values of coked samples vary in between 174 kg/cm^2 to 239 kg/cm^2. From the figure it can be shown that the CCS values of coked samples change in similar fashion with tempered samples where B4 brick gives the best value. The CCS values of coked samples are lowered because of the breaking of the interlocking structure which has been created after polymerization of phenolic resin. The breaking of the interlocking texture was due to the burn out of the total organic portion of the resin.

4.2.3 Modulus of elasticity:

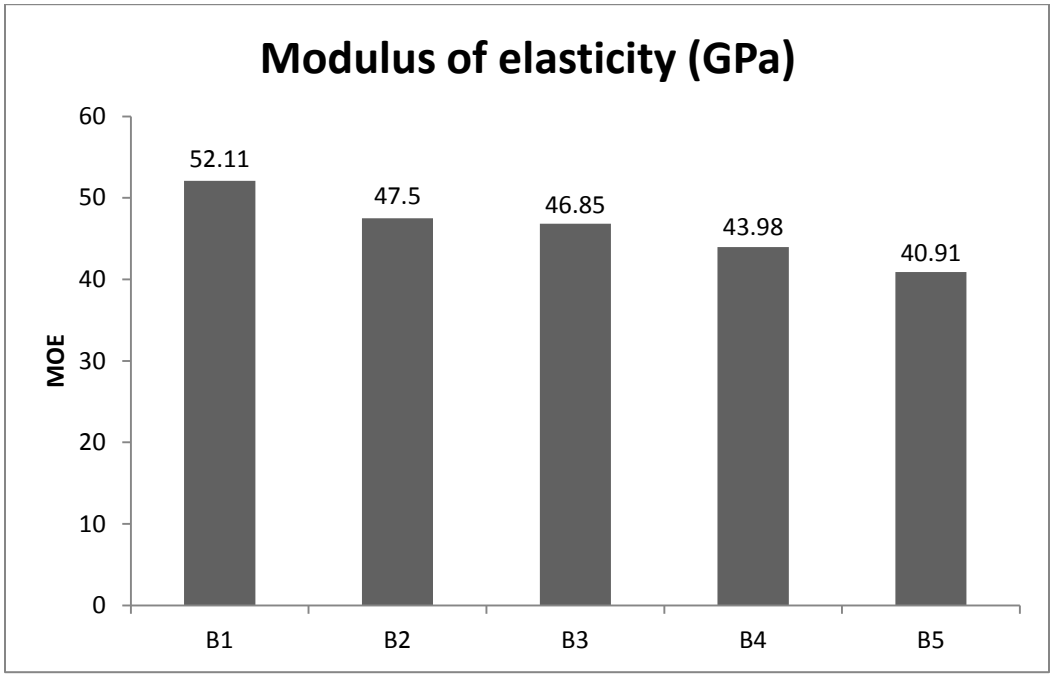

Fig.4.13: Variation of modulus of elasticity with the variation of expanded graphite content

Fig.4.13 shows the variation of MOE with the variation of expanded graphite content. With the increase of expanded graphite percentage MOE decreases almost linearly. MOE values vary within 40.91 GPa to 52.11 GPa. MOE value is highest for the brick which contains no expanded graphite. It is lowest for the B5 brick. As the amount of expanded graphite increases compressibility of the bricks increases which ultimately decreases the MOE value of the bricks.

4.2.4 Hot modulus of rupture:

Comprehensive result is not given in this e-thesis for intellectual property issue. With the increase of expanded graphite pores inside the bricks fill better. So, the strength of the bricks enhances. Because of high surface area, expanded graphite is more reactive than graphite. So, at the high temperature, higher amount of carbide forms by reacting with antioxidants with the increase in expanded graphite.

4.2.5 Thermal shock resistance:

Comprehensive result is not given in this e-thesis for intellectual property issue. Batch 1 shows a good result than batch 2 and 3. Batch 2 and batch 3 shatter after 7^{th} and 8^{th} thermal cycle, whereas the batch 1 sample shatters after 9^{th} thermal cycle. Batch 4 gives the best result which stands 12^{th} thermal shock. But Batch 5 breaks at 12^{th} thermal cycle. Batch 4 and batch 5 shows better thermal shock resistance than others because as the percentage of expanded graphite increases so distribution of carbon into the entire matrix increases.

4.2.6 Oxidation resistance:

Comprehensive result is not given in this e-thesis for intellectual property issue. The variation of the oxidation index of the MgO-C bricks is clear. The oxidation resistance of the brick increases significantly. The oxidation index values decrease with increase in expanded graphite from 69.14% to 40.48%. As expanded graphite forms carbide which has higher oxidation resistance property than that of natural graphite so, the oxidation index decreases with the increase of expanded graphite.

Chapter – 5

Summary and Conclusions

Magnesia-Carbon refractory brick is one of the most important refractories in the steel industry. Magnesia-Carbon bricks have many advantages over the conventional alumina brick lining or alumina / alumina spinel castable linings.

An attempt has been made to reduce the graphite content of the MgO-C refractory by replacing a part of the graphite by expanded graphite in this study. Effect of addition of expanded graphite has been studied in this present work. Total carbon content used for these bricks were 5 wt%. Other raw materials used for this study were fused magnesia, antioxidants (Al and B_4C powder) and resin binder (both liquid and powder). The compositions were mixed and pressed and then various refractory properties were measured for both tempered and cured samples. The effect of expanded graphite was studied by different characteristics of the bricks and the properties were compared with the brick which contained no expanded graphite under similar manufacturing conditions.

The significant features of the new class of refractories fabricated are as follows.

1. The newly fabricated MgO-C refractories exhibited lower apparent porosity. Consumptions as compared to the standard MgO-C refractory (with no EG). For these two compositions, bulk density was also found to increase marginally to 3.05 gm/cc from 2.95 gm/cc for the standard brick.
2. The new compositions exhibited a maximum of 20% increase in the cold crushing strength relative to the standard compositions.
3. Apparent porosity of the coked samples shows progressive lowering in porosity with the amount of EG used, although the coked porosity was lower than

uncoked. Additionally the coked bulk density was found to increase than the standard composition.

4. The trend of CCS for coked samples were similar to those of uncoked samples with two of the new compositions showing ~20% increase in coked CCS.
5. Two of the new compositions exhibited phenomenal increase in HMOR. The increment was almost 80% higher than that of the standard MgO-C refractory.
6. The EG fortified bricks showed progressive decrease in the value of MOE from ~50 to 40 GPa.
7. The new formulations showed excellent thermal shock resistance. While the standard brick failed at 9 air quenching cycles, our composition went past 12 cycles.
8. Dramatic increase in oxidation resistance was observed for the new compositions with an index of ~40% as compared to ~70% for the standard composition.

In totally we have formulated a low carbon MgO-C refractory with 5% graphite with special carbon additives that exhibits excellent thermo-mechanical properties as noted above. Two of the compositions B2 and B3 had either comparable or inferior properties as compared to the standard composition. On the other hand, B4 and B5 exhibited dramatically improved thermo-mechanical properties including HMOR, thermal shock resistance and oxidation resistance.

The technology demonstrated in this work is genetic to carbon/graphite containing refractories in that many of this class of refractories can be strengthened with this approach. This opens up great opportunities to explore new and improved refractory systems.

Scope of future work:

This investigation has opened up a tremendous scope of further research in this direction. The results so far obtained are highly encouraging and may lead to detailed scientific studies. Field trials should be carried out with this club of MgO-C bricks in industrial operational condition. However, the positive effect of addition of expanded graphite to MgO-C refractory has been well-established in this study. A huge potential exists for future commercial application of this study to improve the properties of MgO-C refractories.

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